

PRELIMINARY STUDIES OF THE DYNAMIC MECHANICAL PROPERTIES OF LEATHER* 1587

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ABSTRACT

A forced-vibration resonance method was employed for the first time in studying the dynamic mechanical properties of leather. The response of the free end of a reed-shaped leather specimen that was excited by a sinusoidal displacement at the clamped end was determined. Unsymmetrical resonance curves were obtained, indicating a nonlinearity in dynamic mechanical behavior. It is proposed that this nonlinearity was produced by the fibrous network structure of the leather.



INTRODUCTION

Recently, dynamic mechanical test methods have been utilized with considerable success in relating over-all macroscopic behavior to molecular structure in a wide variety of polymeric systems (1). Little information from this type of test is available for leather (2). Although it is difficult to predict the value of such information, certainly the knowledge gained should contribute to a better understanding of the rather complex system of leather.

Various dynamic test methods have been developed to evaluate the mechanical behavior of polymers over a wide range of speeds, from almost static to megacycles per second. Briefly, the dynamic test methods can roughly be divided into three classes: attenuation methods, resonance methods, and direct stress-strain methods (1). Included in the first class is the wave propagation method employed by Kanagy and Robinson in their studies on leather (1). The frequencies employed in this study varied with the specimen but were in the range of 3000-4000 cycles/second. The results that are to be presented herein were obtained by a method included in the second class, a resonance method which utilized relatively low frequencies from a few cycles to a few hundred cycles per second. Since this method

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has not been previously described in the leather literature, a brief description of the principles involved will be presented.

In the forced-vibration resonance method the mechanical response of a material is measured as a function of applied driving frequency in the vicinity of its natural resonance frequency. Every material so driven has a specific frequency called the resonance frequency at which it undergoes free vibrations, that is, vibrates with a maximum amplitude. At frequencies immediately above and below the resonance frequency the amplitude of vibration decreases. For a linear system the amplitude-of-vibration versus frequency plot is symmetrical, as shown in Fig. 1. The resonance frequency is design-

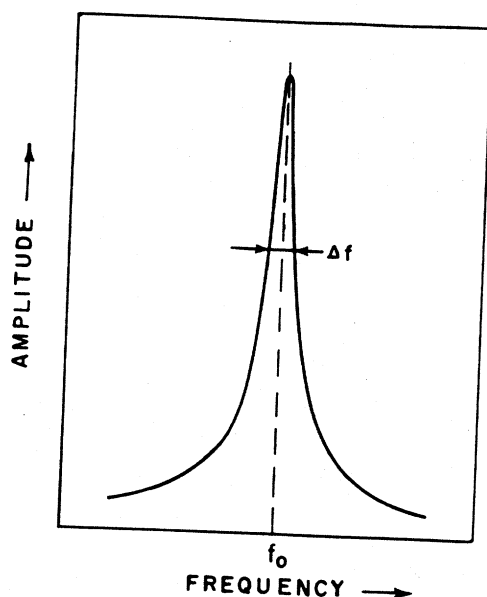


FIGURE 1.—Amplitude-frequency curve for a linear-response material.

nated f_0 , the band width Δf . An analysis of this response curve is required to arrive at the dynamic mechanical properties of the material under investigation. The type of analysis needed depends upon the technique employed.

In the present study, the vibrating reed technique was used. The method consists essentially of a determination of the motion of the free end of a cantilever specimen that is excited by a small sinusoidal displacement at the clamped end. Equations have been derived (3) that relate the resonance frequency and band width of the frequency curve to the real and imaginary

parts of the dynamic modulus of the material. The real part of the dynamic Young's modulus, E , can be calculated using the following expression:

$$E = \frac{48 \pi^2 d l^4}{a_o^4 t^2} f_o^2$$

where d is the bulk density of the specimen, l is length, t is thickness, f_o is the resonance frequency, and a_o is a constant associated with the mode of vibration. For the fundamental vibration $a_o = 1.875$.

The imaginary part of the modulus is associated with internal resistance or friction encountered during dynamic deformation. The internal resistance, η , can be calculated from the relation

$$\eta = \frac{48 \pi^2 d l^4}{a_o^4 t^2} \Delta f$$

where d , l , a_o , and t have the same significance as given above and Δf is the band width or difference between the two frequencies for which the amplitude has 0.707 times its maximum value.

The mechanical response of leather is probably dependent on at least two factors: (a) the viscoelastic properties of the individual fibers, and (b) the character of the network structure that exists as a result of fiber-to-fiber interactions. Therefore it would be desirable to be able to establish a relationship which could account for both effects. Perhaps the proper interpretation of dynamic mechanical test data would provide a means of attaining this goal. In addition, the same information might be of value in establishing a basis for setting up a nondestructive test method for use on whole hides and skins. The work that is being reported was undertaken from these points of view.

EXPERIMENTAL

The vibrating reed apparatus used in the study of the dynamic behavior of leather is schematically illustrated in Fig. 2. It consists of a variable oscillator (Hewlett-Packard 202 CD*) which is capable of generating signals of various strength in the frequency range of 5-600,000 cycles/second. To increase the strength of signal beyond that attainable from the oscillator an amplification system (McGowan Model M-60, 60 watts) is used. The signal is subsequently put into the voice coil of a loudspeaker driver unit (Atlas Sound Corp. Model PD-8VL). An aluminum push rod is connected to the driver unit and transmits sinusoidal motion to a sample clamped at its other end. The amplitude of the free end is measured with a traveling micrometer

*The mention of trade products and firms does not imply their indorsement by the United States Department of Agriculture over similar products or firms not mentioned.

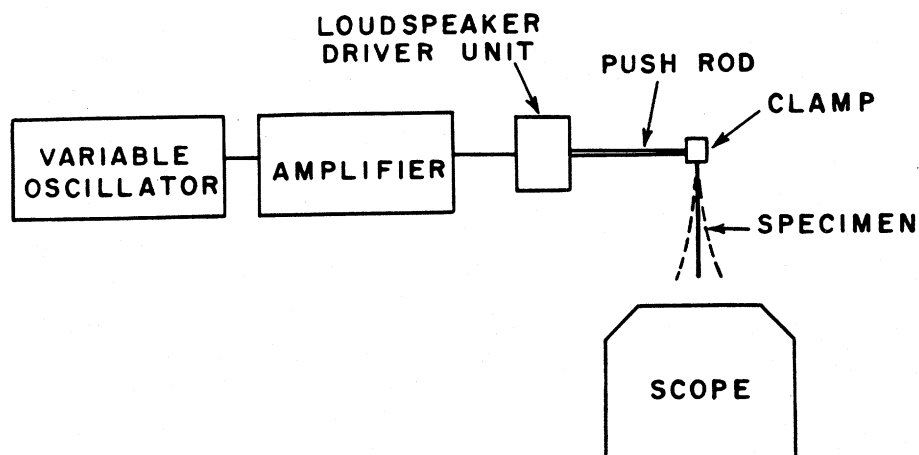


FIGURE 2.—Schematic Illustration of the vibrating reed apparatus.

to $\pm .01$ mm. by observing a magnified image of the vibrating specimen with a 4-power scope.

The data reported herein were obtained using commercially available light leathers. The bulk of the measurements were made on a vegetable-tanned, unfinished calfskin. Specimens used were taken parallel to the backbone in the bend section of the skin. Test specimens were cut so as to have a width of 1 cm. A length of 5 cm. was chosen for making this preliminary study. The natural thickness of the various leather specimens ranged from 0.1 to 0.3 cm.

The measurements were carried out at 73° F. and 50% relative humidity. All specimens were equilibrated at these conditions at least two weeks prior to testing.

RESULTS AND DISCUSSION

Shown in Fig. 3 is the observed amplitude-frequency curve for a vegetable-tanned, unfinished calf. The driving force applied to the specimen at its clamped end was held constant over the employed frequency range, 12 to 25 cycles/sec. The specimen showed a resonance frequency of 16.4 cycles/sec. Particular note of the shape of the response curve should be made. It is not symmetrical. As previously mentioned, the response curve should be essentially symmetrical about the resonance frequency for a linear system. Included in Fig. 3 is the calculated (4) response curve for a linear system with the same resonance frequency and internal resistance. Thus it is quite apparent that under the test conditions employed, the leather specimen exhibited the characteristics of a nonlinear system. Adjacent test specimens of the same skin also produced asymmetric curves.

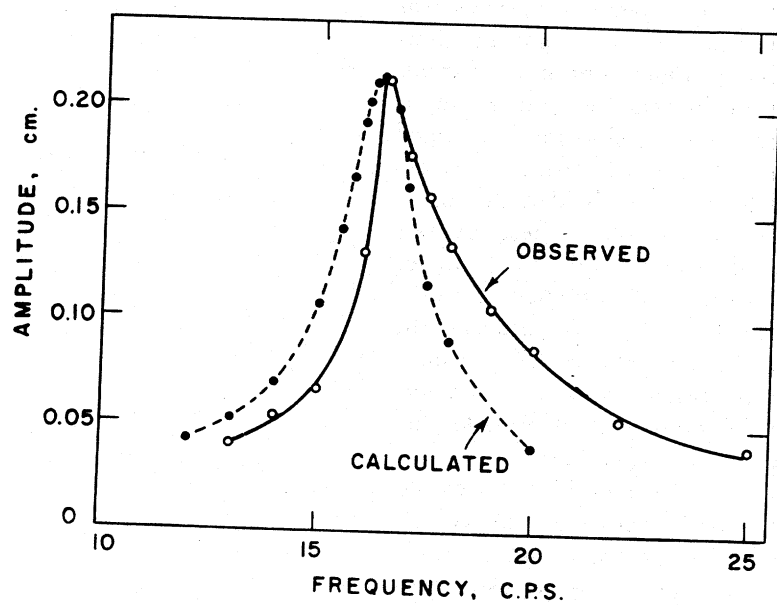


FIGURE 3.—Amplitude-frequency curve of vegetable-tanned unfinished calf.

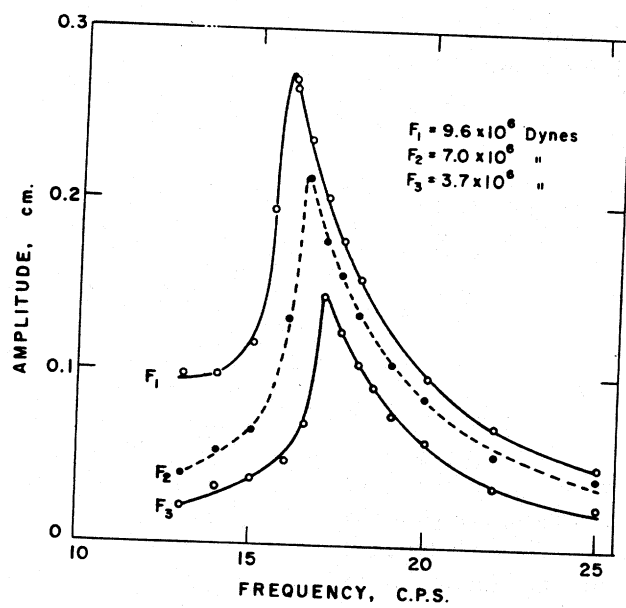


FIGURE 4.—Curves for vegetable-tanned unfinished calf at three different driving forces.

In order to determine whether nonlinearity in dynamic properties was associated with the particular tanned leather studied or was a general characteristic of leather, a number of commercial leathers containing various types and combinations of tanning agents were investigated under similar test conditions. These leathers included vegetable-tanned-chrome-retanned finished calf, chrome-tanned-vegetable-retanned unfinished kip, chrome-tanned-resorcinol-formaldehyde-retanned side leather, and dialdehyde starch-tanned finished calf. The amplitude-frequency curves of all these leathers were asymmetric. However, the curves differed in such details as resonance frequency, amplitude, and band width. A specimen of untanned, acetone-dehydrated calfskin also exhibited nonlinear behavior. Apparently the nonlinearity of the dynamic properties was a characteristic of the system.

A study of the effect of the driving force on the resonance curve was made. Shown in Fig. 4 are the curves for a vegetable-tanned, unfinished leather specimen that were obtained at three different driving forces, $F_1 > F_2 > F_3$. The values of F_1 , F_2 , and F_3 were 9.6×10^6 , 7.0×10^6 and 3.7×10^6 dynes, respectively. The amplitude of vibration at resonance increased with increasing driving force. However, the frequency at which resonance occurred decreased with increasing driving force. If leather were a linear system, the amplitude of vibration would have increased as observed, but the resonance frequency would have remained unchanged. Thus, within the driving force range studied, the leather specimen showed a nonlinearity in dynamic behavior.

The formula previously given for calculating the dynamic bulk modulus of a vibrating specimen showed that the modulus is directly proportional to the square of the resonance frequency. Given in Table I are the calculated

TABLE I
DYNAMIC PROPERTIES OF VEGETABLE-TANNED LEATHER

Driving Force, dynes $\times 10^{-6}$	Dynamic Bulk Modulus, dynes/cm ² $\times 10^{-8}$	Internal Bulk Resistance, dyne/sec/cm ² $\times 10^{-5}$
3.7	2.93	2.4
7.0	2.71	3.2
9.6	2.60	3.6

values for the dynamic bulk modulus and internal resistance at the three driving forces employed. The bulk density of the leather samples was 0.64 as determined from a measurement of weight and volume. The bulk dynamic modulus value increased from 2.60×10^8 dynes/cm² for the largest driving force employed to 2.93×10^8 dynes/cm² for the smallest. In contrast the apparent internal resistance decreased with decreasing driving force.

An explanation for the observed nonlinearity was sought. It is well known that nonlinearity in mechanical response will result if the elastic limit of the material is exceeded. Perhaps the leather specimens under the particular test conditions employed were being strained, at least in part, beyond elastic limit. Calculations of the maximum strain produced in the vibrating specimen at the maximum amplitude of vibration, that is, at resonance, were made, assuming the specimen to be a uniformly loaded cantilever beam. Maximum strains produced at resonance were found to be relatively small, between 0.2 and 0.8%, for the driving forces used. Such small strains were considered well within the elastic limits of the leather. In addition, the same resonance curve was obtained regardless of the number of times the same specimen had been tested or of the direction of approach to the resonance peak. If the specimen had been permanently strained, duplication of the resonance curve should not have been possible. To insure that some factor had not been overlooked, specimens were mechanically conditioned by cyclic loading and tested. These conditioned specimens produced the same type of distorted resonance curves. Therefore, the observed behavior could not be attributed to a nonlinearity of the ordinary stress-strain characteristics of leather.

What other structural characteristic of leather could effect its dynamic mechanical response? Modifications produced within the fibrous network of hide or skin are known to have a marked effect on the mechanical properties of the leather produced. Could the fibrous network be responsible in some manner for the observed behavior? In any one piece of leather there is undoubtedly a large number of fiber-to-fiber interactions. Some of these fiber-to-fiber contacts are probably of such a nature that they are easily altered. Therefore, the number and extent of such contacts might be expected to change with the amplitude of vibration. This would explain the observed nonlinear dynamic behavior of the leather specimens, since a different system of fiber interactions would be produced for each amplitude of vibration.

This distortion of the resonance peaks has been observed for filled rubber compounds. Gehman (5) in a review on the dynamic properties of elastomers points out that the nonlinearity associated with filled rubber compounds has been described as a thixotropic breakdown of the filler structure. The explanation proposed for the behavior of leather is analogous to that proposed for filled rubber. One basic difference between the two systems is the absence of a measurable hysteresis effect in the leather system. Apparently the time required for reforming the original fiber network in leather is relatively short.

If nonlinearity is due to continuously changeable fiber interactions, then it should be possible to cause the specimen to vibrate at such a low amplitude that essentially no fiber interactions would be altered. The specimen would move as a unit and exhibit the characteristics of a linear system. Ap-

parently the dynamic measurements previously discussed were made at too large an amplitude of vibration or strain. Unfortunately, the experimental setup used was not particularly suited for quantitative determination of a complete resonance curve for small amplitudes of vibration. However, it was possible to measure the resonance frequency and amplitude of vibration at resonance for very small driving forces. A series of measurements were made on the same specimen over a relatively large range of driving forces. The bulk dynamic modulus and corresponding maximum percent strain of the specimen were calculated from the data and are given in Fig. 5. The dynamic

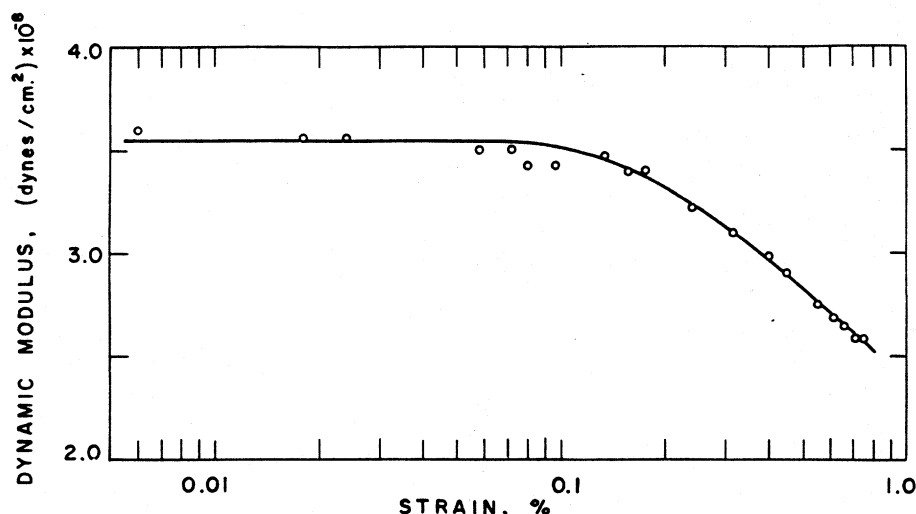


FIGURE 5.—Dynamic modulus-strain curve of vegetable-tanned leather.

modulus increased as the amplitude of the dynamic strain decreased until a strain of approximately 0.1% was reached. Below this strain the dynamic modulus was independent of the strain, indicating that the dynamic behavior of the specimen was essentially linear; practically no change in fiber interactions was produced. The limiting dynamic bulk modulus value obtained from the linear range was about 3.6×10^8 dynes/cm². This compared favorably with the static modulus, 3.7×10^8 dynes/cm², of the same specimen which was measured to torsion.

CONCLUSION

These preliminary results indicate that the forced-vibration resonance method provides a means of obtaining information about the fibrous network structure of leather. Since the type, extent, and number of fiber-to-fiber interactions are altered by chemical modification, fatliquoring, and mechan-

ical working and vary with position in the skin, the potentialities of this dynamic method appear to be great. Many more experimental data are needed, however, before the ultimate value of such studies can be definitely established.

ACKNOWLEDGMENT

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DISCUSSION

PROFESSOR WILLIAM T. RODDY: As Dr. Witnauer has pointed out to us, we now have three different methods of measuring the mechanical properties of leather, namely, the attenuation method reported to our Association in 1955 by Dr. Kanagy, the present method which Dr. Witnauer presented to us today, and finally the stress-strain methods of measuring these properties of leather which have been reported over the years.

Our interest in the present work is the nonlinearity of response exhibited in leather by this particular testing method.

When stress-strain methods are used, they will tend to indicate that leather behaves like other polymeric substances, in that it will give good linear response.

The reasons for these differences might be explained to us today by Dr. Witnauer, if he would care to make a few comments.

DR. WITNAUER: I think that in the direct stress-strain measurement the specimen is being subjected to a different type of mechanical action from the one that I described today. In the vibration method, as the sample swings back and forth, the fibers of leather actually make and break contact with one another. When motion stops, the fibers of the network return essentially

to their original positions. This is time-dependent. If the time interval of the measurements were chosen correctly, you could show this behavior by other tests as well.

PROFESSOR RODDY: Where you use the Tinius-Olsen test, for example, and put a load on the grain and flesh side, and gradually increase the load and then release it, you tend again to get curves that are more linear in character than those obtained by this method.

I would like to ask Dr. Witnauer whether it makes any difference whether the leather in this method is bent grain in or grain out.

DR. WITNAUER: No. We have measured the response with the grain in both directions and observed the same response. In a number of specimens the grain layer was removed, and the specimen still gave the same type of response.

PROFESSOR RODDY: Another point made by Dr. Witnauer is that if you compressed the leather up to a given point and then mechanically between your fingers—or any other way—released this compression and then in turn remeasured the leather, it was found that it behaved much as it would if the compression had not been placed on it. I think we have a similar type of response in the way of stress-strain measurements. As an example, if we do not extend the compressed leather up to anywhere near its breaking load, we shall find that it tends to show little or no permanent fiber change. On the other hand, if we do put too much weight on the specimen and bring it up near its breaking load, then it will no longer respond as it would if it had not been compressed.

Dr. Witnauer has expressed to you that the work is very preliminary and that at the present time he does not have any correlation of this test method with the mechanical properties of leather as they might be used in actual service.